Microemulsions Versus Micelles

LEON M. PRINCE

Lever Brothers Company, Research Center, Edgewater, New Jersey 07020

To differentiate between microemulsions and micellar solutions, an examination was undertaken of the molecular interactions taking place in the interphase of very small droplets. When the interphase is 25 Å thick, there is an abrupt change in the ratio of the volume of the interphase to the volume of the core in the neighborhood of a droplet diameter of 100 Å. Below this diameter, the degree of aggregation, or curvature of the noncoherent interphase, is primarily determined by interactions between water and the heads of the surfactant species. Above this diameter, curvature is determined by specific interactions among oil molecules and surfactant tails as well as by the interactions among the surfactant heads and water in a well-defined coherent interphase. It is such a duplex film, capable of having different tensions at each of its sides, that distinguishes the microemulsion from the micellar solution. A tension or pressure gradient across a freshly formed interphase is able to control its curvature, and thus droplet size, over a much wider range than can the interaction among surfactant heads and water alone.

The data of two of Schulman's alcohol and soap stabilized dispersions were used for this analysis. In one, the oil phase was benzene, in the other hexadecane. It was recalled that as the water content of these inverted micelles was increased, the increase in droplet size was accompanied by an increase in the ratio of alcohol to soap in the interphase. This is important because zero interfacial tension, considered necessary for microemulsions, only occurs at intermediate values of this ratio. In the benzene system this ratio was quickly exceeded, resulting in a macroemulsion at low water content. In the hexadecane system, because of better association between oil molecules and the tails of the surfactant species, the aggregates retained their equilibrium status, despite a high ratio, by changing into cylindrical or lamellar micelles. This behavior was ascribed to a limit in the system of the ratio of alcohol to soap and the amount of oil, suggesting how phospholipids might form liposomes or membrane layers. As more water was added to the lamellar micelles, o/w microemulsions formed providing certain new criteria were met. Emphasis was placed on the choice of components. Because of space limitations in the center of the droplet, long alcohol tails and more than stoichiometric amounts of, or large, cations increased the chances of forming these rare systems. A hypothetical phase equilibria diagram was presented in which the regions of microemulsions, micellar solutions, and liquid crystalline phases were defined qualitatively. In this diagram microemulsions and micellar solutions were distinguished on the basis of aggregate size.

INTRODUCTION

During the past several years there have been proposals that Schulman's fluid, transparent[1], isotropic dispersions of water and oil may not be emulsions at all but swollen

micelles, micellar solutions or micellar emulsions, etc. (1–7). In phase equilibria diagrams these systems were found in the L_1 and L_2 phases, corresponding to normal and inverted phases, respectively. Although on the surface this difference in terminology appears to be only a question of semantics, the matter goes deeper and requires clarification. It is the

[1] Translucent is the general term and includes transparent, which may be described as very translucent.

objective of this study to examine the systems in question in terms of the molecular interactions taking place at the oil/water interface and by so doing, to try to put this question of nomenclature in its proper perspective.

Schulman first called his transparent water-in-oil (w/o) dispersions oleopathic hydromicelles (8), later calling them oleophilic hydromicelles and the oil-in-water (o/w) dispersions hydrophilic oleomicelles (9). Five years later, in his paper with Bowcott (10), Schulman departed from the view that these fine dispersions were micelles and suggested that liquefaction of the mixed interfacial monolayer, by penetration with alcohol or use of a large cation, permitted surface tension gradients across the interphase to effect its curvature and so envelop one liquid in the other in the form of spherical droplets. This was the mechanism proposed by Bancroft 40 yr earlier to explain the formation of (macro) emulsions (11). In 1959, upon learning of the many translucent o/w emulsions of commerce that were transparent or scattered light in the Tyndall range (12) and on the basis of electron micrographs of a series of alkyd emulsions (13, 14), he changed the name of these systems to microemulsions (15).

These o/w microemulsions had a common denominator. They inverted from a w/o to an o/w emulsion by passing through a viscoelastic gel stage consisting of an hexagonal array of water cylinders adjacent to the w/o emulsion and a lamellar phase of swollen bimolecular leaflets adjacent to the o/w emulsion. The liquid crystalline phases of these systems were originally established by optical and x-ray examination (16) and more recently, by optical, conductivity, and NMR studies (17).

THE DATA

For the purpose of our argument, data are presented on two of Schulman's translucent oil and water systems, both of which employed potassium oleate and n-hexanol as the emulsifying agents. In one the oil phase was benzene; in the other it was hexadecane.

In the benzene system, Bowcott and Schulman (10) determined the ratio of the number of molecules of alcohol to soap in the interphase, $(n_a/n_s)_I$. They did this for several ratios of water to soap molecules, n_w/n_s. Using the values of $(n_a/n_s)_I$ corresponding to the several values of n_w/n_s, the diameters of the droplets (internal phase plus interphase) were calculated, assuming areas of 30 Å² for oleate and 20 Å² for alcohol. These data are presented in Table I. When $(n_w/n_s)_I$ exceeded 75, it was no longer possible to clear the system with hexanol.

In contrast, when hexadecane replaced benzene, the system remained clear at $(n_w/n_s)_I$ > 75, passing through a viscoelastic gel stage on the way to inverting to a clear o/w dispersion. Shah and Hamlin (17) identified the compositional points at which the transitions in aggregate form occurred as the ratio of the volume of water to oil, V_w/V_0, increased. The aggregate forms are listed in Table II corresponding to values of V_w/V_0 and n_w/n_s. The value of 3.2 for $(n_a/n_s)_I$ at n_w/n_s of 25 was obtained by Cocke and Schulman (18) in an earlier study of the same system. Using this as a benchmark and by roughly extrapolating the data of Table I, values (in parentheses) were assigned to $(n_a/n_s)_I$ for appropriate values of n_w/n_s. Using these hypothetical

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TABLE II

EFFECT OF WATER ON SWELLING OF HEXADECANE SYSTEM (17)

Point	Aggregate	V_o/V_a[a]	n_w/n_s[b]	$(n_a/n_s)_I$[c]	Droplet diameter, Å
1	Inverted micelle	0.1	8.9	(1)	82
2	w/o microemulsion	0.2	17.8	(2)	96
2a	w/o microemulsion		25	3.2	98
3	w/o microemulsion	0.6	53.4	(5)	122
4	Water cylinders	0.7	62.3		
5	Water cylinders	0.9			
6	Lamellae	1.1			
7	o/w microemulsion	1.3			

[a] 1 ml hexadecane was present in system.
[b] 0.2 g potassium oleate was in system.
[c] 0.4 ml hexanol was in system.

data, diameters of the droplets were calculated as in Table I.

DISCUSSION

This section is divided into three parts: (1) Interpretation of the data; (2) considerations of aggregate size; and (3) a hypothetical phase equilibria diagram. The interconnecting theme is the behavior of the tenants of the interphase.

Interpretation of the Data

To facilitate this discussion a brief review of the theory of emulsions as proposed by Schulman and his coworkers is inserted. It provides a relevant viewpoint not previously presented in this context.

The formation of microemulsions was ascribed to the presence in the interphase of molecules derived from the oil phase (13, 15, 19-21). Intercalated among the soap and alcohol tails, they were seen as developing a high two-dimensional pressure π that depressed the interfacial tension γ_i to zero in accordance with the equation $\gamma_i = (\gamma_{o/w})_o - \pi$, in which $(\gamma_{o/w})_o$ is the oil/water inter-

facial tension after the chemical potential of the alcohol in each phase has been equalized by partitioning. By the terms of this concept zero interfacial tension may only occur at an intermediate value of $(n_a/n_s)_I$. Below this range, π may be high but $(\gamma_{o/w})_o$ has not yet been sufficiently depressed for π to be equal to it. Above this range, the predominantly alcoholic interphase squeezes oil molecules out of it, reducing π below $(\gamma_{o/w})_o$.

Accordingly, it appears that at low water content the value of $(n_a/n_s)_I$ determines the equilibrium status of the system. On this basis, Bowcott and Schulman did not obtain a translucent dispersion when n_w/n_s exceeded 75 because $(n_a/n_s)_I$ was beyond the intermediate range.

This same reasoning explains why the amount of water that their translucent systems could hold was increasingly restricted as the tail of the alcohol was lengthened. Even in the intermediate range of alcohol content, each successive increment of tail length squeezed more benzene molecules out of the interphase until at dodecyl it was no longer possible to develop enough pressure to counteract the tension.

On the other hand, replacement of benzene with hexadecane substantially increased the association of the oil molecules with the tails of the surfactant species. A more highly oriented arrangement of the oil molecules replaced a random type. Thus, a higher alcoholic content was required to squeeze the oil molecules out of the interphase.

The oil molecule-tails association enabled the system to retain its equilibrium over a much wider range of water content. This was accomplished by having the aggregates assume nonspherical forms. At Point 4 in Table II, $(n_a/n_s)_I$ has reached its limit because n_a/n_s is only 5.1. Thus, alcohol molecules are no longer available to expand the water side of the film. Under these circumstances, penetration of the tails by oil molecules at fixed curvature at the head side transforms the spherical aggregates into cylinders of water. As more water is added, this shape persists

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until the supply of oil molecules to fill the tail side of the elongated interphase is exhausted. At this point, presumably Point 6, the association among the tails and hexadecane molecules can no longer prevent a decrease in curvature at the water side of the film and a lamellar form of aggregate results. Such interactions suggest how bimolecular leaflets of aqueous dispersions of phospholipids might form myelin figures (liposomes) or the inner layer of the biological membrane.

Further additions of water effect inversion to an o/w microemulsion providing the system meets certain new criteria. These again involve interactions at both sides of the interphase. Making the tail of the alcohol extraordinarily long assists in forming these o/w systems (15, 19). For example, the o/w microemulsion range of the system of Table II could have been extended had stearyl alcohol instead of hexyl been employed. This would have squeezed oil molecules out of the tail side of the interphase, abetting the wedge formation. By the same token, when twice the stoichiometric amount of a large cation like 2-amino-2-methyl-1-propanol (22) replaces potassium, the wedge is increased by expansion of the head side.

In this perspective, one can define a microemulsion in terms of the molecular interactions in the interphase. At the concentration of alcohol and soap required for zero interfacial tension, the ratio of the volume of surfactants to dispersed phase is also high enough to occupy the volume of interphase needed for droplets less than 2000 Å in diameter. However, zero interfacial tension does not ensure that a microemulsion will form in these systems since cylindrical and lamellar micelles also exist in equilibrium states. What differentiates an emulsion from these liquid crystalline phases is the kind of molecular interaction that produces an initial tension or pressure gradient across the interphase causing it to enclose one bulk phase in the other in the form of spheres. When mechanical work is required to effect such curvature, Bancroft called the system an

emulsion; when the curvature occurs spontaneously, Schulman called the system a microemulsion.

Considerations of Aggregate Size

In these colloidal systems, the degree of light scattering as measured by the naked eye provides a practical means of distinguishing size. Macroemulsions scatter white light. Microemulsions scatter light in the Tyndall range, appearing blue to reflected light and orange-red to transmitted. Although there is some overlapping with microemulsions, micellar solutions do not usually scatter light; they are transparent. There are valid molecular arguments to support such a crude characterization.

These depend on the geometry of very small droplets. In soap stabilized droplets in which the interphase is 25 Å thick, there is a very abrupt decrease in the ratio of the volume of the interphase to the volume of the droplet core, V_I/V_C, in the vicinity of a 100 Å diameter droplet (Table III). This has a decisive influence on the behavior of the interphase. Two kinds of interactions may occur.

In the presence of minimal amounts of water, the heads of the surfactants are drawn together by hydrogen bonding, aggregating them into inverted micelles. The conductivity remains low according to Shah and Hamlin

TABLE III

THE GEOMETRY OF DROPLETS HAVING A 25 Å THICK INTERPHASE

Diameter, Å		$V_I/V_C{}^a$
Core	Droplet	
10	60	215
15	65	80
30	80	18
50	100	7
60	110	5
80	130	3.3
100	150	2.375
1 000	1 050	0.158
10 000	10 050	0.015

^{a} Volume interphase/volume core.

and $(n_a/n_s)_r$ is close to unity. According to Ekwall et al. (5), the water does not behave as a bulk liquid until all hydrogen bonding sites have been occupied. In such a solubilized system, interfacial tension appears to have no meaning. Assuming a water core 10 Å in diameter, V_I/V_C would be 215, from Table III. Since such an interphase would be composed predominantly of oil molecules, the tails of the surfactants would be dissolved in oil. Except for a few oil molecules close to the water interface, oil molecules are randomly oriented among the oleate and hexyl tails. There is really no coherent film in the Langmuir sense. Schulman recognized this in calculating the diameter of the droplets of Table I. By taking the volume of the dispersed phase to include the soap and alcohol it was not necessary to make any assumptions about chain length or orientation except that the interphase be in a completely liquid state. Thus, the driving force that lowers the free energy of the system is the interaction among water molecules and the heads of the surfactant species. This describes a micellar solution. It is submitted that Points 1, 2, and 2a of Table II fall into this category.

When, however, $V_I/V_C < 7$, the behavior of the system depends on the molecular interactions at both sides of a well-defined 25 Å thick interphase. As the ratio of the number of tails to oil molecules increases, the orientation of the oil molecules becomes less random. Since the tails are anchored in the water, orientation is induced among the oil molecules, making for a liquid condensed film. This is particularly so if there is good association among the oil molecules and tails. It is reasonable to assume that such an interphase becomes a duplex film (20), possessing different tensions at each of its sides as the core diameter of the aggregate approaches 50 Å. It is this that differentiates the microemulsion from the micelle. A tension or pressure gradient across a freshly formed interphase is able to control its curvature, and thus droplet size, over a much broader range than can hydrogen bonding among head groups.

These same principles apply to normal micelles and o/w microemulsions. When the amount of oil in the system is very small, the interaction of the surfactant heads with the water phase aggregates the surfactant into normal micelles. The oil is now intercalated among closely packed tails and the volume solubilized in this manner will depend on association with the tails. For a normal micelle to become an o/w microemulsion by increasing in size, there must, as in above, be strong interactions at both sides of a well-defined interphase. In this case, the interactions are much more specific. Because of space limitations in the center of the droplet, sharp wedge formation must be achieved by long alcohol tails squeezing oil molecules away from the core and towards the head side of the interphase. Expansion of the water side of the interphase by increasing the size and number of polar groups associated with the surfactants abets this wedge formation.

Systems in which surfactant species match the oil molecules to effect this kind of wedge formation are extremely rare; the writer has encountered only about 25 such matches in 35 yr experience in the field. It is therefore not surprising that no such system was investigated by means of the phase equilibria diagram. The closest one was a diagram of a nonionic-water-mineral oil system described by LaChampt and Vila (23).

Phase Equilibria Diagram

A phase equilibria diagram would give additional meaning to the foregoing considerations. Figure 1 is a hypothetical diagram in which E (emulsifier) at the apex is the sum of the soap and alcohol. The eight points of Table II serve to delineate the several regions in which the aggregates assume different forms. In defining the region of inverted micellar solutions, the attributes of the six points of Table 1 were taken as guideposts, a liberty justified for illustrative purposes only. The L_2 and L_1 regions include micellar solutions and microemulsions. The macroemulsion re-

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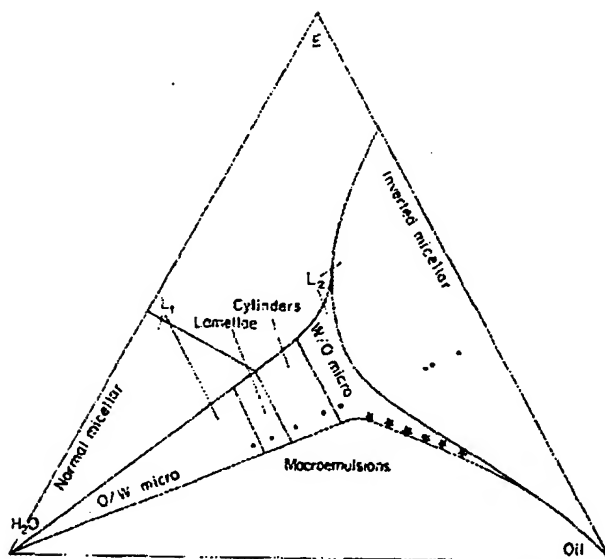
FIG. 1. Hypothetical phase equilibria diagram showing regions of microemulsions and micellar solutions ● are points of Table I; ∗ are points of Table II.

gion lies below the microemulsion region at lower emulsifier content.

The shape of the w/o microemulsion region is unusual. The reason for this is twofold. In systems that invert through a viscoelastic gel stage, e.g., the ones of Table II, dilution with water effects a transition to cylindrical micelles within a very narrow water range. This is how the system maintains its equilibrium. In systems that do not invert, e.g., the ones of Table I, the dispersions are incapable of swelling with more water without losing their equilibrium status, i.e., moving into the macroemulsion region.

The dispersions of Bowcott and Schulman are depicted as being in the microemulsion range in keeping with their droplet size. At lower water content and smaller droplet size they would be micellar solutions. On the other hand, an increase in the level of soap would move them up on the diagram so that they could invert via a viscoelastic gel stage to o/w microemulsions. Benzene-in-water microemulsions have been made in this way.

Unlike the juxtaposition of the inverted micellar solution and w/o microemulsion regions, the normal micellar region lies above the o/w microemulsion region. Dilution of these microemulsions does not change the ratio of emulsifier to dispersed phase so that these systems are infinitely dilutable without changing droplet size. To form normal micellar solutions by decreasing droplet size, the emulsifier content of the system must be increased.

In conclusion, it is submitted that a diagram such as Fig. 1 was not contemplated by the proponents of the micellar solution terminology. The interactions that are needed to form the phases of this diagram are of a higher order of complexity than those required for the phases of Refs. (1–7).

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